

Ozone Formation Sensitivity to Precursors and Lightning in the Tropical Troposphere Based on Airborne Observations

Key Points:

- $\alpha(\text{CH}_3\text{O}_2)$ correlated with NO is a powerful metric for indicating O_3 sensitivity and is valid throughout the troposphere
- O_3 chemistry in the remote tropical lower troposphere is found to be NO_x -sensitive
- NO emissions from lightning drive O_3 sensitivity in the tropical upper troposphere and induce highly VOC-sensitive chemistry

Supporting Information:

Supporting Information may be found in the online version of this article.

Correspondence to:

C. M. Nussbaumer,
clara.nussbaumer@mpic.de

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Author Contributions:

Conceptualization: Clara

M. Nussbaumer, Horst Fischer

Data curation: Clara M. Nussbaumer, Matthias Kohl, Andrea Pozzer, Ivan Tadic, Roland Rohloff, Daniel Marno, Hartwig Harder, Helmut Ziereis, Andreas Zahn, Florian Obersteiner, Andreas Hofzumahaus, Hendrik Fuchs, Christopher Künstler, William H. Brune, Tom B. Ryerson, Jeff Peischl, Chelsea R. Thompson, Ilann Bourgeois

Formal analysis: Clara M. Nussbaumer

Funding acquisition: Jos Lelieveld

Investigation: Clara M. Nussbaumer

Clara M. Nussbaumer¹ , Matthias Kohl¹ , Andrea Pozzer^{1,2} , Ivan Tadic¹, Roland Rohloff¹, Daniel Marno¹, Hartwig Harder¹, Helmut Ziereis³ , Andreas Zahn⁴ , Florian Obersteiner⁴ , Andreas Hofzumahaus⁵ , Hendrik Fuchs⁵, Christopher Künstler⁵, William H. Brune⁶ , Tom B. Ryerson⁷ , Jeff Peischl^{8,9} , Chelsea R. Thompson⁸ , Ilann Bourgeois^{8,9,10}, Jos Lelieveld^{1,2} , and Horst Fischer¹

¹Department of Atmospheric Chemistry, Max Planck Institute for Chemistry, Mainz, Germany, ²Climate and Atmosphere Research Center, The Cyprus Institute, Nicosia, Cyprus, ³Deutsches Zentrum für Luft- und Raumfahrt (DLR), Institut für Physik der Atmosphäre, Oberpfaffenhofen, Germany, ⁴Institute of Meteorology and Climate Research (IMK), Karlsruhe Institute of Technology, Karlsruhe, Germany, ⁵Institute of Energy and Climate Research – Troposphere (IEK-8), Forschungszentrum Jülich GmbH, Jülich, Germany, ⁶Department of Meteorology and Atmospheric Science, Pennsylvania State University, University Park, PA, USA, ⁷Scientific Aviation, Boulder, CO, USA, ⁸National Oceanic and Atmospheric Administration (NOAA) Chemical Sciences Laboratory (CSL), Boulder, CO, USA, ⁹Cooperative Institute for Research in Environmental Sciences, University of Colorado Boulder, Boulder, CO, USA, ¹⁰Now at Université Savoie Mont Blanc, INRAE, CARTELE, Thonon-les-Bains, France

Abstract Tropospheric ozone (O_3) is an important greenhouse gas that is also hazardous to human health. The formation of O_3 is sensitive to the levels of its precursors NO_x ($\equiv \text{NO} + \text{NO}_2$) and peroxy radicals, for example, generated by the oxidation of volatile organic compounds (VOCs). A better understanding of this sensitivity will show how changes in the levels of these trace gases could affect O_3 levels today and in the future, and thus air quality and climate. In this study, we investigate O_3 sensitivity in the tropical troposphere based on in situ observations of NO, HO_2 and O_3 from four research aircraft campaigns between 2015 and 2023. These are OMO (Oxidation Mechanism Observations), ATom (Atmospheric Tomography Mission), CAFE Africa (Chemistry of the Atmosphere Field Experiment in Africa) and CAFE Brazil, in combination with simulations using the EMAC atmospheric chemistry—climate model. We use the metric $\alpha(\text{CH}_3\text{O}_2)$ together with NO to investigate the O_3 formation sensitivity. We show that O_3 formation is generally NO_x -sensitive in the lower and middle tropical troposphere and is in a transition regime in the upper troposphere. By distinguishing observations impacted by lightning or not we show that NO from lightning is the most important driver of O_3 sensitivity in the tropics. NO_x -sensitive chemistry predominates in regions without lightning impact, with α (CH_3O_2) ranging between 0.56 and 0.82 and observed average O_3 levels between 35 and 55 ppbv. Areas affected by lightning exhibit strongly VOC-sensitive O_3 chemistry with $\alpha(\text{CH}_3\text{O}_2)$ of about 1 and average O_3 levels between 55 and 80 ppbv.

Plain Language Summary Ozone (O_3) in the troposphere is both an air pollutant and a greenhouse gas. It is formed from nitrogen oxides (NO_x) and volatile organic compounds (VOCs). The formation can be sensitive to either of these precursors depending on their abundance. Considering the high relevance of O_3 in regard to human health and global warming, it is important to understand this sensitivity of O_3 formation, which allows to predict future changes in O_3 . Here, we investigate O_3 formation sensitivity toward NO_x and VOCs in the tropical troposphere based on aircraft measurements during four research campaigns between 2015 and 2023, and a global model. We include observations of NO, HO_2 (hydroperoxyl radicals) and O_3 over South America, the Middle East and the Pacific, Atlantic and Indian Ocean. We find that O_3 formation is sensitive to NO_x in the lower tropical troposphere. In the upper tropical troposphere, lightning events control O_3 chemistry and promote strong VOC-sensitive O_3 formation.

1. Introduction

Ozone (O_3) in the stratosphere is essential to life on this planet through its shielding of the Earth's surface from the sun's shortwave radiation (Staehelin et al., 2001). In contrast, in the troposphere O_3 has adverse effects for plants, human health and the climate (Ainsworth et al., 2012; Nuvolone et al., 2018). O_3 is an important anthropogenic greenhouse gas (after CO_2 and CH_4). Its impact on global warming is strongest in the upper troposphere. At these

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Project administration: Jos Lelieveld, Horst Fischer
Supervision: Horst Fischer
Visualization: Clara M. Nussbaumer
Writing – original draft: Clara M. Nussbaumer
Writing – review & editing: Clara M. Nussbaumer, Matthias Kohl, Andrea Pozzer, Ivan Tadic, Hartwig Harder, Helmut Ziereis, Andreas Zahn, Florian Obersteiner, Andreas Hofzumahaus, Hendrik Fuchs, Jeff Peischl, Jos Lelieveld, Horst Fischer

altitudes, O₃ is most abundant (relative to tropospheric levels), temperatures are coldest and concentrations of water vapor, the predominant natural greenhouse gas, are low (Cooper et al., 2014; Iglesias-Suarez et al., 2018; IPCC, 2023). This influence of O₃ on the radiative budget is particularly pronounced in tropical latitudes (30°S to 30°N), which are characterized by large O₃ precursor emissions due to strong lightning and particularly low temperatures due to the high altitude of the tropical tropopause (Iglesias-Suarez et al., 2018; Lacis et al., 1990; Skeie et al., 2020). O₃ is additionally an important precursor for OH radicals, which in turn control the atmospheric oxidizing capacity (Lelieveld et al., 2016).

Primary sources of ozone in the troposphere include transport from the stratosphere and photochemical formation. While the exact source distribution has not yet been fully understood up to this point, it is almost certain that photochemical production is the dominant source of O₃ in the troposphere (Archibald et al., 2020; Cooper et al., 2014; Lelieveld & Dentener, 2000). Nitrogen oxides (NO_x ≡ NO + NO₂) and volatile organic compounds (VOCs) are photochemical precursors for O₃ in the troposphere. NO_x is mostly emitted in the form of NO and converted to NO₂ in the presence of peroxy radicals (mostly HO₂ and CH₃O₂), shown in Reactions R1 and R2. Peroxy radicals in turn are formed through oxidation of VOCs or carbon monoxide (CO) by OH radicals (Crutzen, 1988; Nussbaumer & Cohen, 2020; Pusede et al., 2015).



NO₂ forms O₃ in the presence of sunlight and oxygen from the air via Reaction R3.



Precursor sources at the surface are combustion processes (vehicle engines, vessels, industrial activities, etc.), biomass burning and soil emissions for NO and mostly evaporative emissions, including volatile chemical products (personal care products, detergents, etc.), as well as biogenic emissions from vegetated areas for VOCs (McDonald et al., 2018; Pusede et al., 2015). Aircraft and lightning are sources of NO at higher altitudes in the troposphere.

Depending on the precursor concentrations, O₃ formation can be sensitive to either NO_x or VOCs, the latter represented by peroxy radicals. A detailed analysis and discussion of our current understanding of O₃ sensitivity can be found in Nussbaumer et al. (2023). Briefly, for low NO_x, referred to as NO_x-sensitive O₃ chemistry, VOCs and therefore peroxy radicals are present in excess. Peroxy radicals undergo Reactions R1 and R2 with NO and further react with themselves in radical recombination reactions or undergo auto oxidation. O₃ formation generally increases with increasing NO. O₃ chemistry is VOC-sensitive when NO_x is available in excess. A maximum level of ozone production is reached when the available peroxy radicals react with NO to form NO₂. The impact of increases in NO_x on O₃ concentrations for VOC-sensitive O₃ chemistry changes with the altitude, which we hypothesize is due to the fraction of NO₂. At the surface, O₃ formation decreases with increasing NO_x due to the reaction of OH radicals with NO₂ (instead of VOCs to generate peroxy radicals), which becomes relevant when NO_x is more abundant than reactive VOCs. Observations of decreasing O₃ at high NO_x are often reported in literature, for example, Nussbaumer and Cohen (2020), Sicard et al. (2020) or Gough and Anderson (2022). In the upper troposphere, the reaction of NO₂ with OH only plays a minor role—likely because daytime NO₂ is low as the NO_x equilibrium is shifted toward NO. Consequently, O₃ is much less responsive to NO changes. We have shown this effect of O₃ in the upper troposphere in Nussbaumer et al. (2023).

In order to understand and predict the response of O₃ toward changes in NO_x and VOCs, it is essential to investigate which precursor O₃ is sensitive to, given its importance for air quality and climate. Various metrics exist to determine which sensitivity prevails, including the response of ozone production P(O₃) to changes in NO_x, the weekend effect, the HCHO to NO₂ ratio, the HNO₃ to H₂O₂ ratio and the LNO_x to LRO_x ratio. As described in the previous paragraph, P(O₃) increases with NO_x for NO_x-sensitive and decreases with NO_x for VOC-sensitive O₃ chemistry. The driver for the latter decrease is the increasing importance of the (HO_x cycle) terminating reaction NO₂ + OH with increasing NO_x. This context is used when investigating the weekend effect (e.g., Fujita et al. (2003); Gough and Anderson (2022)). A smaller number of transporter trucks and commuter

traffic during weekends leads to lower NO_x concentrations. When O_3 reductions are observed along these NO_x conditions, O_3 formation is NO_x -sensitive. In contrast, O_3 enhancements on weekends indicate VOC-sensitive chemistry. The metric HCHO/NO_2 represents the ratio of VOCs and NO_x (e.g., Sillman (1995); Tonnesen and Dennis (2000)). High values indicate the prevalence of VOCs and, therefore, NO_x -sensitive O_3 chemistry. Low values highlight the increased availability of NO_x and VOC-sensitive O_3 formation. The HCHO/NO_2 ratio requires knowledge about experimental thresholds for each sensitivity region. For example, Duncan et al. (2010) suggest $\text{HCHO}/\text{NO}_2 < 1$ for VOC-sensitive and $\text{HCHO}/\text{NO}_2 > 2$ for NO_x -sensitive O_3 formation. The $\text{HNO}_3/\text{H}_2\text{O}_2$ ratio compares the two major termination pathways of the HO_x cycle (e.g., Sillman (1995); Sillman and He (2002); Vermeuel et al. (2019)). These are the loss of NO_2 via the reaction with OH (forming HNO_3) and the loss of HO_2 via self-reaction (forming H_2O_2). The prevalence of NO_x promotes the termination via NO_2 loss, representing VOC-sensitive O_3 chemistry. The termination via HO_2 recombination becomes dominant for prevailing VOCs over NO_x , indicating NO_x -sensitive O_3 chemistry. An extension of $\text{HNO}_3/\text{H}_2\text{O}_2$ is given by the $\text{LNO}_x/\text{LRO}_x$ ratio, which compares the loss of NO_x (LNO_x) with the loss of RO_x (LRO_x) (e.g., Schroeder et al., 2017; Sourì et al., 2020, 2023). The loss of NO_x is hereby given by the reaction of NO_2 with OH and is equal to considering the formation of HNO_3 . In addition to the formation of H_2O_2 via HO_2 , the loss of RO_x includes the self-reaction of RO_2 and the cross-combination of HO_2 and RO_2 . Similar to the ratios HCHO/NO_2 and $\text{HNO}_3/\text{H}_2\text{O}_2$, an experimental threshold is needed to identify the transition point, for example, $\text{LNO}_x/\text{LRO}_x \sim 2.7$ as given by Sourì et al. (2020). Studies by Schroeder et al. (2017) and Sourì et al. (2023) indicate that difficulties in the use of HCHO/NO_2 can be addressed by the application of $\text{LNO}_x/\text{LRO}_x$, which they found to be superior for the identification of near surface ozone formation sensitivity. A detailed review and comparison of the most common metrics in the literature is presented in Liu and Shi (2021) for the surface and Nussbaumer et al. (2023) for the global troposphere. We found that most of these metrics are only applicable at the surface, and particularly not in the upper troposphere. Mixing ratios of trace gases vary significantly throughout the troposphere and definitions for the surface, for example, $\text{P}(\text{O}_3)$ changes with NO_x or experimental thresholds for the HCHO/NO_2 , $\text{HNO}_3/\text{H}_2\text{O}_2$ or $\text{LNO}_x/\text{LRO}_x$ ratios might not apply at high altitudes. $\text{P}(\text{O}_3)$, $\text{HNO}_3/\text{H}_2\text{O}_2$ and $\text{LNO}_x/\text{LRO}_x$ consider the dominance of the terminating reaction $\text{NO}_2 + \text{OH}$ (forming HNO_3) as an indicator for VOC-sensitive O_3 chemistry. At high altitudes, NO_2 concentrations tend to be low and so does the NO_x loss via the pressure-dependent reaction $\text{NO}_2 + \text{OH} (+\text{M})$. As a consequence, we hypothesize that $\text{P}(\text{O}_3)$ as a function of NO increases beyond the transition point between NO_x - and VOC-sensitive O_3 formation sensitivity in the upper troposphere. We have shown this in Figure S10 of Nussbaumer et al. (2023), which presents $\text{P}(\text{O}_3)$ and $\text{L}(\text{NO}_x)$ versus NO for upper tropical tropospheric data simulated by the general circulation model EMAC. The loss of NO_x via $\text{NO}_2 + \text{OH}$ is less than 5% of $\text{P}(\text{O}_3)$ over the entire range of NO from 0 to 1 ppbv. Therefore, $\text{L}(\text{NO}_x)$ does not impact the course of $\text{P}(\text{O}_3)$ as a function of NO and it can therefore not indicate the transition from NO_x - to VOC-sensitivity. The same applies to $\text{HNO}_3/\text{H}_2\text{O}_2$ and $\text{LNO}_x/\text{LRO}_x$. Further drawbacks of these metrics at high altitudes are that knowledge of NO_2 mixing ratios is required, which does not allow for the application of in situ measurements. It was shown that NO_2 measurements in the upper troposphere suffer from thermal artifacts from peroxy nitrates, independent of the measurement principle (Shah et al., 2023). Instead, we have developed a new metric, $\alpha(\text{CH}_3\text{O}_2)$, to determine O_3 sensitivity, which is valid throughout the entire troposphere (Nussbaumer et al., 2021a, 2022). $\alpha(\text{CH}_3\text{O}_2)$ presents the ratio of methyl peroxy radicals CH_3O_2 (a proxy for VOCs) which react with NO and promote O_3 formation in competition with the peroxy radical self-reaction which inhibits O_3 formation. O_3 formation is NO_x -sensitive when $\alpha(\text{CH}_3\text{O}_2)$ increases with increasing NO. In this case, peroxy radicals are present in excess, and O_3 production is sensitive only to changes in NO (NO_x -sensitive). O_3 chemistry is VOC-sensitive when $\alpha(\text{CH}_3\text{O}_2)$ and, at the same time O_3 formation, become unresponsive to changes in NO. Instead, O_3 production is sensitive only to changes in VOCs (VOC-sensitive) and, consequently, peroxy radicals. We present more details including the calculation of $\alpha(\text{CH}_3\text{O}_2)$ in Section 2.1. $\alpha(\text{CH}_3\text{O}_2)$ indicates the transition from NO_x - to VOC-sensitive O_3 formation sensitivity at around 0.1 ppbv NO for Figure S10 in Nussbaumer et al. (2023).

$\alpha(\text{CH}_3\text{O}_2)$ was originally proposed as an indicator for formaldehyde formation and applied to three stationary ground-site measurements across Europe in Cyprus, Germany and Finland (Nussbaumer, Crowley, et al., 2021). $\alpha(\text{CH}_3\text{O}_2)$ identified NO_x -sensitive O_3 chemistry in southeastern Europe and VOC-sensitive O_3 chemistry in central Europe, which is in line with results obtained via the HCHO to NO_2 ratio, a metric dating back to studies by Sillman (1995). In Nussbaumer et al. (2022), we used $\alpha(\text{CH}_3\text{O}_2)$ to indicate a change in upper tropospheric O_3 sensitivity in response to reduced air traffic (and a 55% reduction in NO_x mixing ratios) during the COVID-19 lockdowns over Europe, which common metrics would have failed to identify. We have recently investigated

O₃ sensitivity in the upper tropical troposphere based on modeling simulations by a general circulation model and found lightning as the most important driver of VOC-sensitive O₃ chemistry (Nussbaumer et al., 2023). Generally, these studies have underlined that NO_x is most relevant in O₃ formation and sensitivity and that the abundance of VOCs only plays a subordinate role.

There are numerous studies that have investigated O₃ sensitivity to NO_x and VOC levels at the surface and they almost exclusively focus on urban areas (Akimoto & Tanimoto, 2022; Jaffe et al., 2022; Li et al., 2019; Zhao et al., 2022). While this is highly relevant with respect to air quality and human health, it is also important to investigate more remote locations particularly in regard to future emission changes. For example, with increasing temperatures and decreasing precipitation one could expect to see increases in biomass burning, resulting in emission of NO_x in the remote rainforest (Bray et al., 2021). In combination with the high levels of VOCs in these areas, O₃ could increase drastically locally, and in turn harm the natural vegetation and agricultural crops (Ainsworth et al., 2012; Pope et al., 2020). At the same time, ongoing industrialization in the Global South will likely impact ozone concentrations in the tropical troposphere (Gaudel et al., 2024). In contrast to surface-based analyzes, research on O₃ sensitivity in the upper troposphere is scant and has not been investigated in detail since the studies of Brasseur et al. (1996), Jaegl  et al. (1998), Wennberg et al. (1998), and Jaegl  et al. (1999) around 25 years ago, who concluded that O₃ chemistry was NO_x-sensitive in the upper troposphere over the United States based on box-model simulations. Of note, the observations for high NO_x did not match the model predictions in Jaegl  et al. (1998, 1999). We suggest that O₃ production is an unsuitable metric for indicating O₃ sensitivity at high altitudes. This could be (partly) due to the terminating reaction OH + NO₂ (forming HNO₃), which does not seem to play a significant role for low NO₂ mixing ratios in the upper troposphere. Findings by Jaegl  et al. (1998, 1999) and Nussbaumer et al. (2023) suggest that P(O₃) is an unsuitable indicator for determining O₃ formation sensitivity at high tropospheric altitudes.

This study investigates O₃ chemistry in the tropical troposphere based on airborne observations during four aircraft campaigns, namely OMO, ATom, CAFE Africa and CAFE Brazil, between 2015 and 2023. We compare in situ observations with modeled data by the ECHAM5/MESSy2 Atmospheric Chemistry (EMAC) model and we investigate the differences in trace gas concentrations and vertical profiles between the individual campaigns (and regions). We use $\alpha(\text{CH}_3\text{O}_2)$ to identify O₃ sensitivity towards its precursors in the tropical troposphere, with a particular focus on the role of lightning.

While we have previously analyzed O₃ chemistry in the upper tropical troposphere based on model simulations (Nussbaumer et al., 2023), this is the first study to investigate the question of O₃ sensitivity at these altitudes based on in situ observations using the metric $\alpha(\text{CH}_3\text{O}_2)$. To our knowledge, $\alpha(\text{CH}_3\text{O}_2)$ is currently the only available metric reliably indicating which precursor O₃ is sensitive to at altitudes at which common tools fail and the impact of O₃ as a greenhouse gas is strongest.

2. Observation and Methods

2.1. O₃ Sensitivity Metric $\alpha(\text{CH}_3\text{O}_2)$

$\alpha(\text{CH}_3\text{O}_2)$ was originally developed for identifying HCHO (formaldehyde) production pathways. It presents the share of CH₃O₂ (methyl peroxy radicals) reacting with NO or OH radicals forming HCHO versus the peroxy self-reaction (CH₃O₂ + HO₂) forming CH₃OOH (Nussbaumer, Crowley, et al., 2021). The reaction of CH₃O₂ with NO also yields NO₂, which forms O₃ via Reaction R3. The pathway of CH₃O₂ with NO forming methyl nitrate is negligibly small and does not impact O₃ formation. The reaction of CH₃O₂ with HO₂ represents a termination reaction of the O₃ formation process (which is relevant for a low-NO_x environment). The reaction of CH₃O₂ with OH contributes to HCHO, but not to O₃ formation, and generally only plays a minor role compared to the pathway via NO and HO₂. Therefore, it can be disregarded when studying O₃ sensitivity. Hence, $\alpha(\text{CH}_3\text{O}_2)$ is calculated via Equation R4. We only use positive values for determining $\alpha(\text{CH}_3\text{O}_2)$ to ensure that the resulting value is between 0 and 1. The rate constants k were obtained from the IUPAC database with $k(\text{CH}_3\text{O}_2 + \text{HO}_2) = 3.8 \times 10^{-13} \exp(780/T)$ and $k(\text{CH}_3\text{O}_2 + \text{NO}) = 2.3 \times 10^{-12} \exp(360/T)$. T represents the ambient temperature in Kelvin (IUPAC, 2024).

$$\alpha(\text{CH}_3\text{O}_2) = \frac{k_{\text{CH}_3\text{O}_2+\text{NO}} \times [\text{NO}]}{k_{\text{CH}_3\text{O}_2+\text{NO}} \times [\text{NO}] + k_{\text{CH}_3\text{O}_2+\text{HO}_2} \times [\text{HO}_2]} \quad (\text{R4})$$

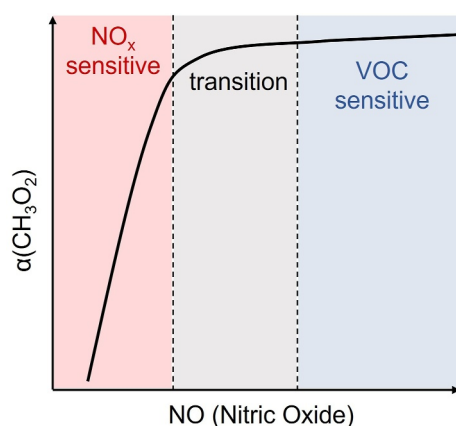


Figure 1. Identifying the dominant O_3 sensitivity using $\alpha(CH_3O_2)$ (adapted from Nussbaumer, 2023). This is a simplified overview for explanation purposes. The absolute numbers for $\alpha(CH_3O_2)$ and NO vary depending on the studied region.

A detailed description of $\alpha(CH_3O_2)$ can be found in Nussbaumer, Crowley, et al. (2021), Nussbaumer et al. (2022), and Nussbaumer et al. (2023). Briefly, for low NO_x concentrations, CH_3O_2 react with both NO and HO_2 and increases in NO lead to increases in $\alpha(CH_3O_2)$. O_3 chemistry is NO_x -sensitive. For high NO_x concentrations, most available CH_3O_2 reacts with NO and changes in NO have no impact on $\alpha(CH_3O_2)$, as O_3 sensitivity is limited by the availability of peroxy radicals (which represent the abundance of VOCs). Figure 1 schematically shows how to use $\alpha(CH_3O_2)$ to identify prevailing O_3 sensitivity (Nussbaumer, 2023). O_3 concentrations increase with increasing NO_x when O_3 chemistry is NO_x -sensitive. For VOC-sensitive O_3 chemistry at the surface, O_3 formation decreases with increasing NO_x due to the reaction of OH and NO_2 . In the upper troposphere, O_3 concentrations reach a maximum and remain unresponsive to changes in NO_x . $\alpha(CH_3O_2)$ is currently the only available metric that identifies O_3 formation sensitivity based on in situ observations throughout the troposphere. While HO_2 measurements remain to be a challenge, uncertainties will only impact the exact definition of the transition point between NO_x - and VOC-sensitive O_3 formation, which does not affect the overall result.

2.2. Aircraft Campaigns

Figure 2 presents an overview of the flight tracks of the four research aircraft campaigns discussed in this paper. These are OMO (Oxidation Mechanism Observations), ATom (Atmospheric Tomography Mission), CAFE Africa (Chemistry of the Atmosphere Field Experiment in Africa) and CAFE Brazil. The ATom campaign was divided into measurements over the Atlantic and the Pacific Ocean. Detailed information on the individual campaigns and the respective measurements are provided in the following subsections. We filtered all data for the tropical latitudes between $30^\circ S$ and $30^\circ N$ and for the troposphere with a threshold of 100 ppbv for O_3 . We use a 1-min average of the measurements, brought to the NO timestamp, for this analysis.

2.2.1. OMO 2015

The aircraft campaign OMO (Oxidation Mechanism Observations) took place in July and August 2015 over the Indian Ocean and the Middle East using the HALO (High Altitude LONG range) research aircraft. The campaign comprised 17 research flights (some on the same day) with campaign bases in Paphos in Cyprus ($34.72^\circ N$, $32.49^\circ E$) and Gan in the Maldives ($0.69^\circ S$, $73.16^\circ E$). More details can be found in Lelieveld et al. (2018) and Tomsche et al. (2019). Nitric oxide was measured via chemiluminescence with the two-channel AENEAS (Atmospheric nitrogen oxides measuring system) instrument with a detection limit of 7 pptv and a measurement uncertainty of 8% (for 0.5 ppbv) (Stratmann et al., 2016; Ziereis et al., 2000). HO_2 was measured via laser-induced fluorescence with the HORUS (Hydroxyl Radical Measurement Unit based on fluorescence Spectroscopy) and the AirLIF instruments (Künstler, 2020; Marno et al., 2020; Novelli et al., 2014). The HORUS instrument has a detection limit of 1.2 pptv for HO_2 at the surface and 0.23 pptv above 14 km. The accuracy is typically between 20% and 40%. The detection limit and uncertainty for the Air-LIF instrument are also altitude-dependent. The

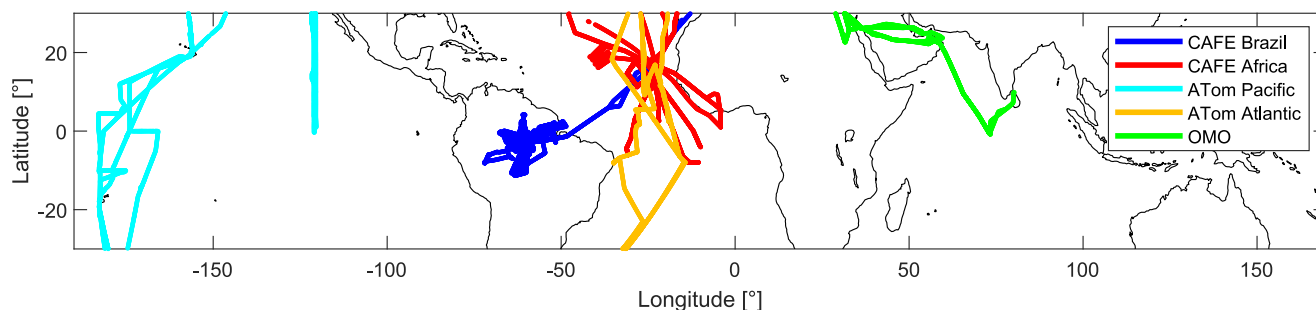


Figure 2. Overview of the flight tracks (filtered by tropical latitudes between $30^\circ S$ and $30^\circ N$) for the four aircraft campaigns OMO (green), ATom, CAFE Africa (red) and CAFE Brazil (blue). The ATom campaign was separated into data over the Atlantic (orange) and the Pacific Ocean (cyan).

detection limit (signal-to-noise ratio = 2, 40 s time resolution) is generally less than 1 pptv and about 0.1 pptv above 5 km. The data accuracy is between 15% and 35%. Neither of the HO₂ measurements was continuous over the entire campaign. The data from the five overlapping flights showed good agreement and we therefore combined the data from the two instruments (research flights 1–6 (21.07.–06.08.2015) from AirLIF and 7–17 (08.08.–27.08.2015) from HORUS) to obtain a full data set. Ozone was measured with the FAIRO (Fast AIRborne Ozone) instrument using a dry chemiluminescence detector, calibrated by a 2-channel UV photometer, with an uncertainty (10 Hz) of 2.5% or 2 ppbv (Obersteiner, 2023; Zahn et al., 2012).

2.2.2. ATom 2016–2018

The aircraft campaign ATom (Atmospheric Tomography Mission) consisted of four deployments between 2016 and 2018 in summer 2016, winter 2017, fall 2017 and spring 2018 with the NASA DC-8 aircraft, operated by the NASA Armstrong (Dryden) Flight Research Center. A total of 47 scientific flights were carried out over the almost 2-year period. Each deployment circumnavigated the globe once. More details on the campaign, including all flight tracks, can be found in Thompson et al. (2022) and via the campaign website (NASA, 2022). For this study, we used the data measured in the tropical regions between 30°S and 30°N latitude and additionally separated them into two geographic regions over the Pacific and the Atlantic Ocean (see Figure 2 in cyan and orange, respectively). NO and O₃ were measured via chemiluminescence using an O₃-induced and a NO-induced technique, respectively. The measurement uncertainties (1 Hz data) were 5% for NO and 2% for O₃, with a precision of 6 pptv and 15 pptv, respectively (Bourgeois et al., 2021, 2022). HO₂ was measured via laser-induced fluorescence with a 2 σ accuracy of 35%. Details can be found in Faloona et al. (2004).

2.2.3. CAFE Africa 2018

The Chemistry of the Atmosphere Field Experiment in Africa (CAFE Africa) took place in August and September 2018 from Sal on Cabo Verde (16.75°N, 22.95°W). Fourteen scientific flights were performed with the HALO research aircraft, mostly over the Atlantic Ocean. Details on the campaign and measurements can be found in Tadic et al. (2021). Nitric oxide was measured with the chemiluminescence instrument (CLD 790 SR, ECO Physics, Dürnten, Switzerland) NOAH (Nitrogen Oxides Analyzer for HALO) with a detection limit of 5 pptv (1 min) and an uncertainty of 6%. The instrument is described in detail in Tadic et al. (2020) and Nussbaumer, Parchatka, et al. (2021). Ozone was measured with the FAIRO instrument, as described in Section 2.2.1. HO₂ was measured with the HORUS instrument and has an uncertainty of approximately 50%. Due to the difficulty in determining an experimental calibration factor for the HO₂ data set, a value of 2.5 was estimated based on comparison with the EMAC model and its performance in measuring hydrogen peroxide (H₂O₂) (Hamryszyk et al., 2023).

2.2.4. CAFE Brazil 2022–2023

The Chemistry of the Atmosphere Field Experiment in Brazil (CAFE Brazil) took place in December 2022 and January 2023 with the HALO research aircraft from Manaus in Brazil (3.03°S, 60.04°W). Twenty scientific flights (including four transfer flights from Oberpfaffenhofen, Germany with a stopover in Sal, Cabo Verde) were carried out over a 2-month period over the pristine rain forest as well as deforested regions and urbanized areas. The scientific goals of the campaign included the investigation of photochemical processes impacted by high VOC/low NO_x environments, convective events throughout the troposphere and particle formation. The campaign was timed to occur at the seasonal transition which enabled capture of measurements during the dry season in December and the rainy season in January. Nitric oxide was measured with the NOAH instrument with a detection limit of 6 pptv (1 min) and an uncertainty of 5%. O₃ data were obtained with the FAIRO instrument with a data uncertainty of 2.5% or 2 ppbv. Final data for HO₂ measurements are not available at this point and we therefore include modeled data from EMAC simulations, as described in Section 2.3 in our analysis.

2.3. Modeling

While this study is based on in situ observations, we include the modeled data for a comparison to identify how well the data sets align. Additionally, we use modeled HO₂ data for CAFE Brazil as final experimental data are not available at this point.

Modeled data for NO, O₃, HO₂, temperature, and pressure were obtained with the EMAC model. The ECHAM/MESSy Atmospheric Chemistry (EMAC) model is a numerical chemistry and climate simulation system that includes sub-models describing tropospheric and middle atmosphere processes and their interaction with oceans, land and human influences (Jöckel et al., 2016). It uses the second version of the Modular Earth Submodel System (MESSy2) to link multi-institutional computer codes. The core atmospheric model is the fifth generation European Centre Hamburg general circulation model (Roeckner et al., 2006, ECHAM5). The physics subroutines of the original ECHAM code have been modularized and reimplemented as MESSy submodels and have continuously been further developed. Only the spectral transform core, the flux-form semi-Lagrangian large scale advection scheme, and the nudging routines for Newtonian relaxation are remaining from ECHAM. Here we use different numerical results from different integrations and with different set-up, mostly presented in previous publications. Description of the set-up of the EMAC model for CAFE Africa, OMO, and ATom campaigns can be found in Tadic et al. (2021), Lelieveld et al. (2018), and Nussbaumer et al. (2023), respectively.

The simulation for the CAFE Brazil measurement campaign was performed at a spectral horizontal resolution of T63, equivalent to approximately 180 × 180 km at the equator, with 90 vertical levels up to an altitude of 0.01 hPa. Weak “nudging” was applied, guiding the simulation toward meteorological reanalysis data (ERA5, Hersbach et al., 2020) from the European Centre for Medium-Range weather forecasts (ECMWF). Global anthropogenic emissions of reactive gases and aerosols at the surface were obtained from the Community Emission Data System (CEDS, McDuffie et al., 2020) and aircraft emission data were taken from the CAMS Global aviation emissions (CAMS-GLOB-AIR; Granier et al., 2019), both for the year 2019.

The simulations for OMO, ATom and CAFE Africa present the same horizontal resolution as the CAFE Brazil simulation, that is, T63. On the other hand, 47 hybrid pressure levels were used to cover the same vertical extension up to 0.01 hPa (instead of 90 levels for CAFE Brazil). In the work of Tadic et al. (2021) and Lelieveld et al. (2018) for CAFE Africa and OMO, respectively, the anthropogenic emissions from EDGARv4.3.2 (Crippa et al., 2018) were used. In Nussbaumer et al. (2023), used for comparison with the ATom observations, the long-term anthropogenic emission data set of CAMS-GLOB-ANTv4.2 (Granier et al., 2019) was adopted. Furthermore, in both the work of Tadic et al. (2021) and Lelieveld et al. (2018), a complex oxidation scheme (MOM) was employed, which has been extensively evaluated in Pozzer et al. (2022). In the work of Nussbaumer et al. (2023) the MIM oxidation scheme was adopted (Pöschl et al., 2000; Taraborrelli et al., 2009). The same algorithms for dry and wet deposition (Kerkweg et al., 2006; Tost et al., 2006) were used in all simulations. Importantly, while the same parameterization was used for lightning NO_x (Grewe et al., 2001), different scaling factors were employed (Tost et al., 2007). For the ATom and CAFE Africa simulations a total emission of ~6.2 Tg N yr⁻¹ was used, in accordance with Miyazaki et al. (2014). In contrast, for the OMO simulation a similar amount as for CAFE Brazil was implemented, that is, ~2.6 Tg N yr⁻¹, which demonstrates the best agreement with regional observations. These values fall within the estimate of 2–8 Tg N yr⁻¹ provided by Schumann and Huntrieser (2007).

3. Results

3.1. Model Performance

Figure 3 shows a normalized Taylor diagram presenting the model performance for each campaign and trace gas investigated in this analysis (Taylor, 2001). The experimental data is represented by the black hexagram, with a normalized standard deviation of 1, a correlation coefficient of 1 and root-mean-square difference of 0. The closer the colored data points, representing the model data sets, are located to the experimental reference value, the better the model performance. For most of the modeled data sets, standard deviations are similar to those from their experimental counterparts. Deviations are observed for NO (blue): CAFE Brazil (triangles) and OMO data sets (squares) have lower standard deviations by a factor of 2 and the CAFE Africa data set (circles) has a larger standard deviation (almost twice as large). The latter additionally shows only an intermediate correlation coefficient of around 0.3. All other modeled data sets show a good correlation with the experiment with a correlation coefficient of 0.5 or larger. The ATom data set (diamonds) for O₃ even reaches values of >0.8. The O₃ (red) and HO₂ data sets (cyan) for the different campaigns show a similar model performance, whereas differences could be seen between the quality of the different NO data sets. This could be due to the difficulty in accurately representing lightning in the model. A further comparison between modeled and measured data can be found in Figures S1–S5 in Supporting Information S1, where we show the vertical profiles of each trace gas. Tables S1–S5 in

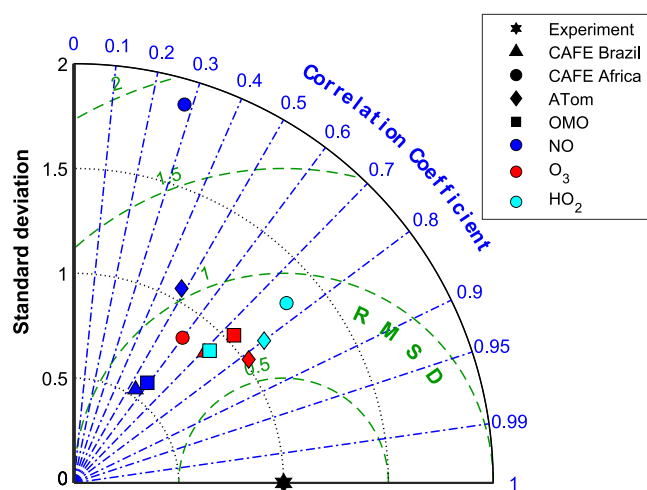


Figure 3. Overview of the model performance, presented in a Taylor diagram (Taylor, 2001). The normalized standard deviation is indicated by the black dotted lines, the correlation coefficient is presented by the blue lines and the root-mean-square difference is shown by the green dotted lines. The black hexagram represents the experimental data. Triangles represent modeled data for the CAFE Brazil campaign, circles the CAFE Africa campaign, diamonds the ATom campaign and squares show modeled data for the OMO campaign. Blue colors represent NO, red shows O₃, and HO₂ data is cyan. The closer the modeled data points are located to the experimental comparison, the better the model performance.

Supporting Information S1 show an overview of the number of data points per altitude bin used to create the vertical profiles. The model may have difficulties representing the intermittent nature of convection and lightning, illustrated by the larger spread in the upper troposphere (UT). HO₂ modeled and experimental vertical profiles align well for OMO, CAFE Africa, and ATom and the Taylor diagram also shows a good model performance, which verifies the use of the modeled HO₂ data set for CAFE Brazil.

3.2. Vertical Distribution

Figure 4 presents the vertical profiles of (a) NO, (b) O₃, and (c) HO₂ measured during the investigated campaigns. During CAFE Brazil, CAFE Africa and ATom over the Pacific and the Atlantic Ocean, NO was low in the lower and middle troposphere with median values below 20 pptv up to 8 km altitude. The values during the OMO campaign were much larger up to 5–6 km; however, only around 5% of all data points were measured at these low altitudes and they were exclusively located in proximity to airports. Therefore, it can be assumed that the large NO mixing ratios represent localized airport emissions. At high altitudes, the profiles show elevated mixing ratios. Above 10 km, NO median values were overall highest during CAFE Africa with 117 pptv, followed by OMO with 108 pptv and CAFE Brazil with 60 pptv. These campaigns were also characterized by large maximum values for NO, sometimes above 1 or 2 ppbv, which indicates strong lightning activity. Median and peak values were generally lower during the ATom campaign with mixing ratios of 51 pptv and 0.43 ppbv, respectively, over the Atlantic and only 20 pptv and 0.48 ppbv, respectively, over the Pacific Ocean. These

observations underline the impact of lightning at these altitudes and latitudes. We have determined a filter for lightning activity which defines data points above 2 km with NO mixing ratios above 100 pptv as impacted by lightning. This includes both fresh and aged lightning emissions. We have tested the performance of this filter via two different methods. First, we investigated NO mixing ratios simulated by the EMAC model as a daily climatology between 2000 and 2020 across all tropical latitudes and altitudes. We filtered for data points between 800 and 200 hPa and with values above 0.1 ppbv. To identify data points above the threshold which did not arise from lightning, we extracted the corresponding data points in a modeled data set excluding lightning emissions.

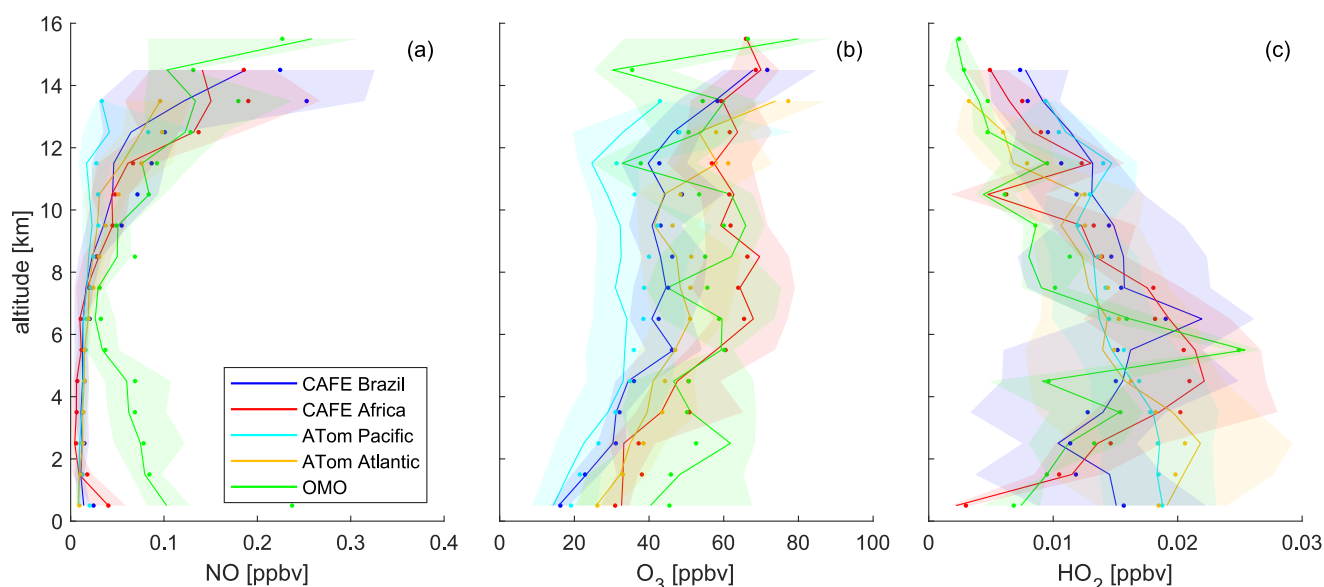


Figure 4. Vertical profiles of (a) NO, (b) O₃, and (c) HO₂ for tropical latitudes for the investigated aircraft campaigns. Lines and shades represent the median values and the 25th/75th percentiles, respectively. Dots show the mean values in the center of each 1 km altitude bin.

Less than 2% of the remaining data points were larger than 0.1 ppbv. Second, we tested the impact of convective updraft from pollution events, such as wildfires or shipping emissions. For this, we identified data points for which CO was 1.5 or 2 σ larger than the average at the respective altitude (bins of 1 km). We compared the share of data points identified as lightning by the filter, including and excluding enhanced CO, and did not find significant differences (deviation <5%). These tests confirm the suitability of the chosen filter. For OMO, this identifies approximately 50% of the data points as being impacted by lightning, followed by CAFE Africa with around 40% and CAFE Brazil with approximately 20%. For ATom, only few data points were impacted by lightning with below 10% over the Atlantic Ocean and less than 5% over the Pacific Ocean, the latter explaining the almost unchanging (with altitude) cyan vertical profile.

These observations demonstrate two important features impacting lightning, which are the time of year and the distance from tropical landmasses. The maximum of deep convection, which is associated with lightning activity and large NO emissions, changes its location throughout the year due to seasonal, meridional changes in convective activity. While over the year as a whole, this maximum is located close to the equator ($\pm 5^\circ$), in January, it is mostly found in the Southern Hemisphere and in July in the Northern Hemisphere (compare Figure 12 in Yan (2005)). The region of maximum deep convection is also referred to as the ITCZ (Inter Tropical Convergence Zone). CAFE Africa and OMO were carried out in August/September mostly coinciding with the location of the ITCZ, explaining high lightning intensity. CAFE Brazil took place in December and January and the flight track latitudes tended to be slightly northward, but still close to the location of the ITCZ at that time of the year, which could be a potential explanation for fewer data points with identified lightning impact. The impact of the time of year can be neglected for the ATom campaign as the vertical profiles present medians and averages across all four deployments. Lightning was lowest over the remote Pacific Ocean during ATom, in line with our understanding of lightning formation, which is thought to require solid particles for the formation of light ice particles. In fact, solid particles, such as dust or sand, are usually more abundant over or in proximity to land masses, which makes lightning strongest over the (tropical) continents (Christian et al., 2003; Nussbaumer, Tadic, et al., 2021; Verma et al., 2021). Pan et al. (2022) presented that sea spray particles could even inhibit lightning activity over oceans. Likewise, low lightning activity was observed over the Atlantic Ocean during ATom. The NO observations for CAFE Africa were much larger in comparison to the ATom Atlantic data in the upper troposphere, although the two data sets are derived from neighboring geographical areas. The location of the ITCZ throughout the year cannot explain the difference, as the median NO mixing ratios measured during the ATom deployment in August were similar to the one in February. However, the ATom Atlantic data set shrinks when filtering the tropical latitudes for different times of the year, whereas CAFE Africa ran many flights in the same region and therefore provides an improved representation of the region. Additional differences may arise from meteorological conditions or differences in wildfire activity between years (ATom Atlantic in August 2016 and CAFE Africa in August 2018).

Figure 4b presents the vertical profiles of O₃. Generally, O₃ increased with altitude and increasing proximity to the stratosphere, where O₃ is abundant. The lowest mixing ratios were observed during ATom over the Pacific Ocean with median values below 17 ppbv at the surface and 28 ppbv above 10 km. This correlates well with low NO mixing ratios throughout the tropospheric column, which when oxidized to NO₂ is the photochemical source of tropospheric O₃. The low mixing ratio between 11 and 12 km altitude could indicate convective updraft from the O₃-poor marine boundary layer. CAFE Brazil O₃ mixing ratios were similar to those observed during ATom Pacific up to 5 km altitude. Above this altitude, O₃ median values during CAFE Brazil were approximately 10–14 ppbv higher. The vertical profile also shows the typical S-shape observed for convective updraft to the upper troposphere. The ATom Atlantic O₃ vertical profile shows a similar shape to the one observed during CAFE Brazil with median mixing ratios of 26 ppbv at the surface and 52 ppbv above 10 km. The vertical O₃ profile for OMO does not show a particular trend with altitude, but a quite strong fluctuation with median values between 30 and 80 ppbv is evident. O₃ mixing ratios during CAFE Africa were around 30 ppbv (median) at the surface and increased strongly up to 60–70 ppbv at 7 km, above which they remained mostly unaffected by altitude. The large difference of around 20 ppbv between O₃ mixing ratios for CAFE Africa and ATom Atlantic in the free troposphere could have likely arisen from the time of year as the profiles align well when only considering August data from the ATom campaign. This could be due to wildfire emissions in the Southern Hemisphere at that time of year.

Figure 4c presents the vertical profiles of HO₂. Mixing ratios were mostly low and comparable to upper tropospheric values at the surface and showed a maximum in the free troposphere between 3 and 7 km altitude. Quite

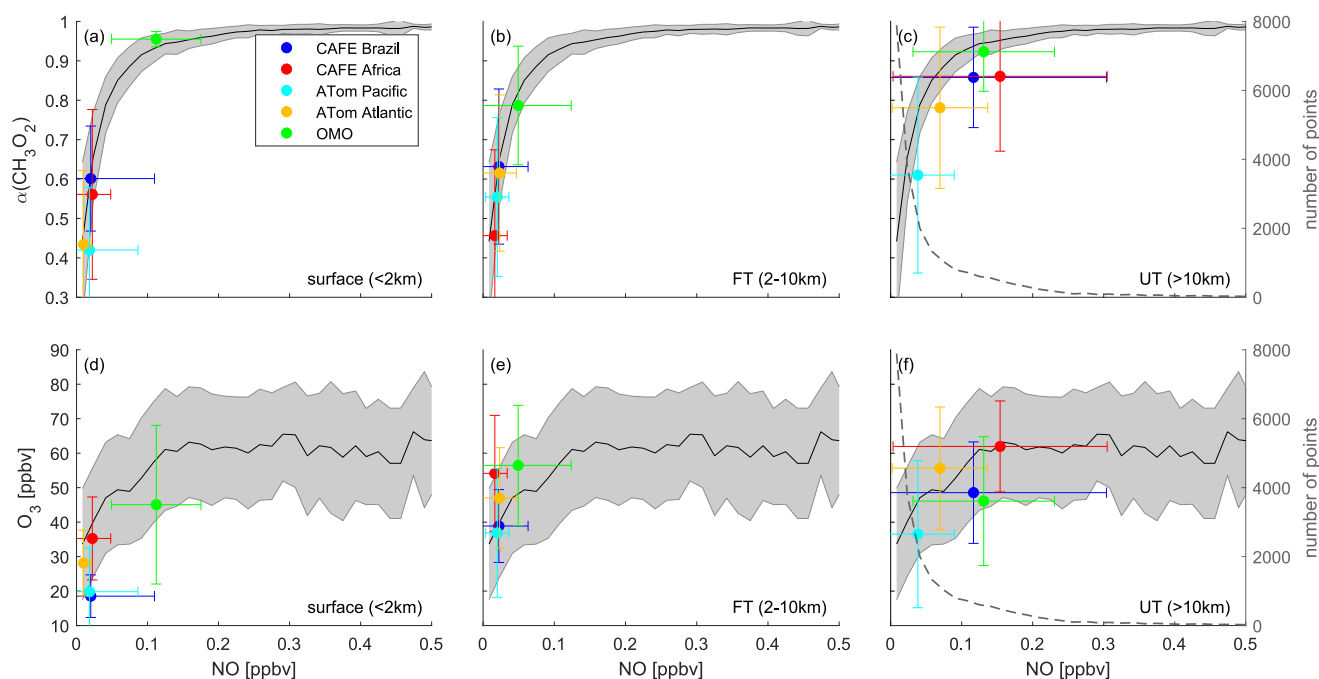


Figure 5. Overview of determination of O_3 sensitivity via (a)–(c) $\alpha(CH_3O_2)$ and (d)–(f) O_3 versus NO mixing ratios separated into the surface below 2 km (a and d), the free troposphere between 2 and 10 km (b and e) and the upper troposphere above 10 km (c and f). Black lines represent the tropical background as an average of all available data points binned to NO, with 1σ standard deviations shown as gray areas. The colored data points and error bars present the campaign averages and 1σ standard deviations, respectively. CAFE Brazil averages are shown in blue, CAFE Africa in red, ATom Pacific in cyan, ATom Atlantic in orange and OMO in green. The gray dotted line in panels (c) and (f) shows the number of data points in each NO bin.

large differences between the campaigns can be observed at the surface with median values ranging from around 2 pptv for CAFE Africa and approximately 20 pptv for ATom. However, the uncertainties of the HO_2 measurements were usually highest at low altitudes and the profiles mostly show large and overlapping error shades (representing the 25th and 75th percentiles). In the upper troposphere, HO_2 measured during OMO and ATom Atlantic was lowest with a median of 4 pptv above 12 km, followed by CAFE Africa with 7 pptv and CAFE Brazil and ATom Pacific with 10–11 pptv.

3.3. O_3 Sensitivity

As described above, $\alpha(CH_3O_2)$ can be used to determine O_3 sensitivity to its precursors. $\alpha(CH_3O_2)$ is plotted in Figure 5a–5c for all campaigns. The black line shows the average $\alpha(CH_3O_2)$ binned to NO mixing ratios for all available data points and therefore presents the tropical “background.” The individual curves for each campaign do not show significant differences. As expected, $\alpha(CH_3O_2)$ increases strongly with NO for low ambient NO mixing ratios, which demonstrates NO_x -sensitive O_3 chemistry. For an increase in NO from 10 to 100 pptv, $\alpha(CH_3O_2)$ increases by almost 0.5. For higher NO, $\alpha(CH_3O_2)$ becomes unresponsive to changes in NO, which is characteristic of VOC-sensitive O_3 chemistry. For an NO increase from 100 to 500 pptv, $\alpha(CH_3O_2)$ shows an increase of less than 0.1. Panel (c) additionally shows the number of data points in each NO bin by the gray dashed line. The vast majority of the data points is characterized by NO mixing ratios below 0.1 ppbv. The number decreases to a few dozen data points for the high-NO bins. The colored data points represent the campaign averages and the three panels of each row show different altitudes. Figure 5 (a) presents the averages below 2 km altitude. CAFE Brazil, CAFE Africa, ATom Pacific and ATom Atlantic showed a clear NO_x -sensitive chemistry at the surface, as the averages are located in the rising part of the background curve of $\alpha(CH_3O_2)$ versus NO. Average values for $\alpha(CH_3O_2)$ were around 0.4 for ATom and close to 0.6 for CAFE Africa and CAFE Brazil, which means that 60% and 40%, respectively, of the available peroxy radicals reacted with HO_2 and terminated the O_3 -forming HO_x cycle. This is expected given low NO mixing ratios in the remote tropical regions or over tropical waters. The OMO data set showed VOC-sensitive O_3 chemistry at the surface with $\alpha(CH_3O_2) = 0.96$, indicating that almost all peroxy radicals reacted with NO instead of HO_2 . However, as mentioned above, the very

limited number of data points available at low altitude for the OMO campaign were all captured in proximity to airports and therefore do not represent surface conditions in the Middle East or over the Indian Ocean. Figure 5b shows the results for the free troposphere between 2 and 10 km altitude. All campaigns showed a clear NO_x -sensitive O_3 chemistry, which again is expected in the absence of NO sources at these altitudes and aligns with the observations from the vertical profiles in Figure 4. In Figure 5c, upper tropospheric data (above 10 km) are presented. The upper troposphere over the remote Pacific Ocean was clearly NO_x -sensitive. The remaining areas were located in a transition regime with average values for $\alpha(\text{CH}_3\text{O}_2)$ of between 0.78 and 0.92 and for NO of between 0.07 and 0.15 ppbv, whereby ATom Atlantic tended toward NO_x sensitivity and the remaining campaigns toward VOC-sensitive O_3 chemistry. The data points additionally show a large 1σ standard deviation in the order of 100% for NO. This underlines the large variability of NO mixing ratios in the upper troposphere caused by clean NO-free air transported from the boundary layer via convective processes and strong, local NO emissions from lightning. We identified <5% and <10% of data points as being impacted by lightning for ATom Pacific and ATom Atlantic, respectively, demonstrating NO_x -sensitive chemistry. For the remaining campaigns, lightning impacted a much higher share of data points (~20% for CAFE Brazil, ~40% for CAFE Africa and ~50% for OMO), resulting in higher values for $\alpha(\text{CH}_3\text{O}_2)$.

These observations are confirmed when looking at O_3 versus NO mixing ratios as displayed in the lower panels (d)–(f) of Figure 5. The black line and gray error shading represent background O_3 binned to NO, including all available data points. For NO_x -sensitive chemistry approximately up to 0.1–0.15 ppbv NO, O_3 increases from 30 to 60 ppbv with increasing NO. Our hypothesis is that in this rising part both peroxy self-reaction and NO to NO_2 oxidation via peroxy radicals play a significant role, the latter path leading to O_3 formation in the presence of sunlight and oxygen. With increasing amounts of NO, O_3 levels rise. In turn, when NO is present in excess over peroxy radicals, O_3 levels reach a maximum, as its formation is limited by the availability of peroxy radicals. At the surface, as shown in Figure 5d, O_3 average values for CAFE Brazil, CAFE Africa, ATom Atlantic and ATom Pacific were low, ranging from 20 to 35 ppbv. O_3 for OMO was higher which correlated with higher NO captured from airport emissions. Slightly higher O_3 levels between 35 and 55 ppbv were observed for the free troposphere, which can be seen in Figure 5e. These elevated values compared to the surface cannot be explained by photochemical formation in the NO-poor free troposphere, but are likely rather an outcome of transport processes. Upper tropospheric values for O_3 versus NO are presented in Figure 5f and show similar features compared to $\alpha(\text{CH}_3\text{O}_2)$ in panel (c). Low average O_3 (37 ppbv) and NO (0.04 ppbv) indicate NO_x -sensitive chemistry in the upper troposphere over the remote Pacific Ocean during the ATom campaign. The remaining data points were located mostly in the transition area. Maximum average values of O_3 of >60 ppbv were observed for CAFE Africa, going hand-in-hand with high shares of lightning-impacted data. In contrast, O_3 average values for ATom Atlantic (56 ppbv) were much higher than those observed for OMO (46 ppbv), even though less than 10% of the data points were impacted by lightning during ATom versus 50% during OMO. While the correlation of O_3 with NO can provide valuable hints for sensitivity investigations, it cannot be solely captured by photochemistry. Instead, O_3 could also be impacted by transport from the stratosphere or regions with strong tropospheric ozone buildup, for example, biomass burning events, and has a longer upper tropospheric lifetime than NO. The O_3 -NO correlation should therefore be used in combination with a reliable metric such as $\alpha(\text{CH}_3\text{O}_2)$.

3.4. Impact of Lightning

We have investigated the role of lightning in O_3 sensitivity by applying a filter for lightning impact. We categorize data points above 2 km altitude and with NO mixing ratios higher than 0.1 ppbv as impacted by lightning. If the observed NO value is lower, we assume that the data point was not directly impacted by lightning. We expect the contribution of aircraft to the overall NO_x emissions in the tropical troposphere to be insignificant (Grewe, 2007; Nussbaumer et al., 2023). Figure 6 presents the O_3 sensitivity analysis based on $\alpha(\text{CH}_3\text{O}_2)$ and O_3 versus NO, following the similar scheme as in Figure 5, separated into data points impacted and not impacted by lightning. The share of data points in each average value depends on the campaign, for example, for ATom Pacific more than 95% fall into the category without lightning, whereas it is 50% for OMO. The background curves are the same as those presented in Figure 5.

Figure 6a shows $\alpha(\text{CH}_3\text{O}_2)$ versus NO for data points without lightning impact. All five campaign averages were located in the rising part of the background curve with values for $\alpha(\text{CH}_3\text{O}_2)$ between 0.56 and 0.82, indicating distinct NO_x -sensitive O_3 chemistry. In comparison, Figure 6b presents data points with lightning impact. In all cases, independent of the latitude, $\alpha(\text{CH}_3\text{O}_2)$ was high and close to 1. This shows that available peroxy radicals

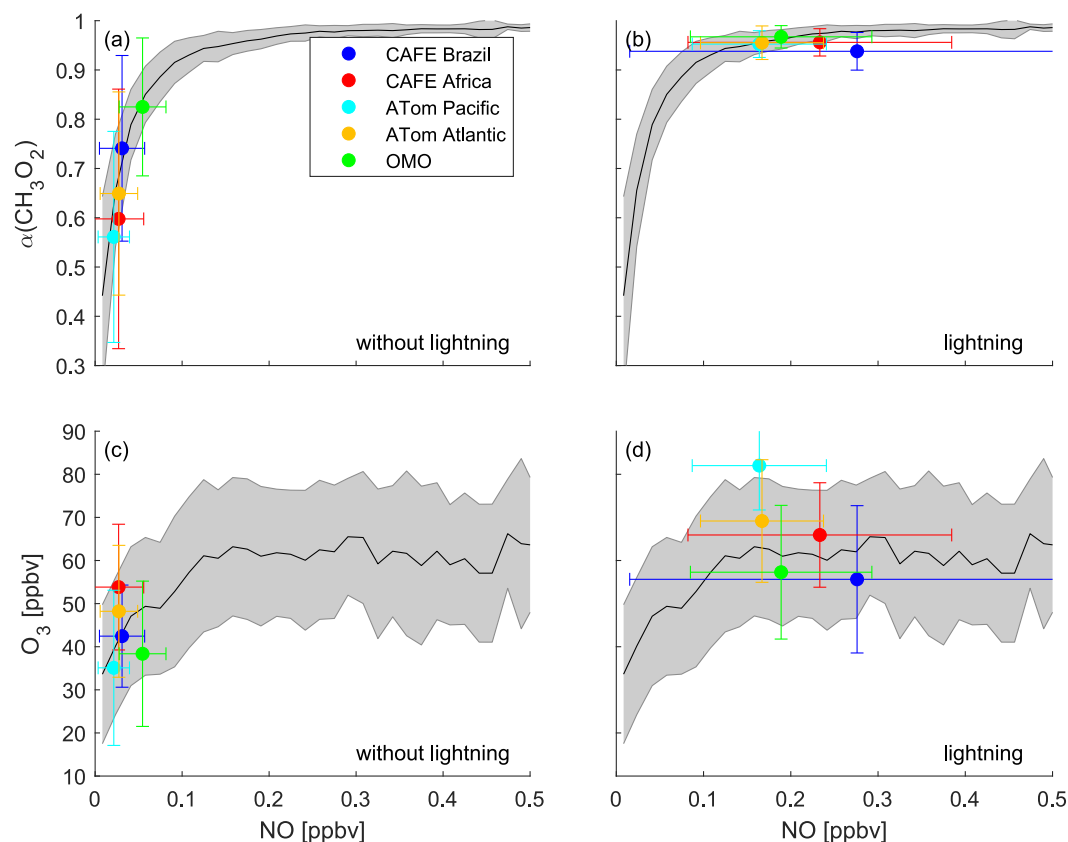


Figure 6. Overview of determination of O_3 sensitivity via (a)–(b) $\alpha(\text{CH}_3\text{O}_2)$ and (c)–(d) O_3 versus NO mixing ratios separated into data with (b and d) and without impact from lightning (a and c).

dominantly reacted with NO resulting in the formation of O_3 , indicating VOC-sensitive chemistry. The 1 σ standard deviations (shown by the error bars) are quite large because lightning induces highly variable amounts of NO and additionally, we do not distinguish between fresh and aged lightning in this view. For CAFE Brazil, for example, we observed peak values of more than 2 ppbv NO (factor 4 compared to the shown scale).

Figure 6c shows O_3 versus NO for data points not impacted by lightning. O_3 average values ranged between 35 and 55 ppbv. In comparison, the average values impacted by lightning were located at much higher O_3 mixing ratios (between 55 and 80 ppbv) and in the part of the background where O_3 becomes unresponsive to NO , as shown in panel (d). These results support the findings from $\alpha(\text{CH}_3\text{O}_2)$ and show that lightning plays an important role in the sensitivity of O_3 formation toward its precursors.

4. Conclusion and Outlook

In this study, we presented in situ measurements of NO , O_3 and HO_2 from four different research aircraft campaigns in the tropical troposphere. These are the OMO campaign in 2015 over the Middle East and the Indian Ocean, the CAFE Africa campaign in 2018 over the Atlantic Ocean, the ATom campaign between 2016 and 2018 around the American continent and the CAFE Brazil campaign in 2022/23 over Brazil. We separated the ATom campaign into a part over the remote Pacific Ocean and a part over the Atlantic Ocean. All data is filtered for the troposphere (<100 ppbv O_3) and for tropical latitudes (30°S – 30°N). We compared the in situ measurements with modeled data by the ECHAM5/MESSy2 Atmospheric Chemistry (EMAC) model and found good agreement with a correlation coefficient mostly ranging between 0.5 and 0.8 and standard deviations mostly similar to the respective experimental data set. The largest discrepancies were found for the modeled NO for CAFE Africa. Based on these findings, we used the HO_2 modeled data for CAFE Brazil, as final experimental data were not available. We found low mixing ratios for NO at the surface and in the free troposphere across the remote tropical latitudes, underlining the absence of sources at these altitudes. Mixing ratios in the upper troposphere were

elevated compared to the lower altitudes with highest values over tropical continents (compared to tropical waters), and coincided with the location of maximum deep convection and the ITCZ, where lightning activity peaks. HO₂ was mostly similar in the campaign inter-comparison and large variability made it difficult to identify significant differences. O₃ vertical profiles show signs of deep convective processes, especially for the CAFE Brazil campaign. Mixing ratios were lowest over the remote Pacific Ocean and higher for areas impacted by emissions, for example, biomass burning, such as CAFE Africa.

We investigated O₃ sensitivity using O₃ mixing ratios and the metric $\alpha(\text{CH}_3\text{O}_2)$ correlated with ambient NO. We found that O₃ chemistry at the surface and the free troposphere was almost exclusively sensitive to NO_x. The only exception was the OMO campaign, where we observed VOC-sensitive O₃ chemistry at the surface due to the capture of anthropogenic pollution from airports. For the upper troposphere, we found NO_x-sensitive O₃ chemistry over the remote Pacific Ocean during ATom and a transition regime for the other campaigns, with the value for $\alpha(\text{CH}_3\text{O}_2)$ increasing with the amount of lightning observed. Separating data points with and without lightning impact showed that lightning is the most important factor controlling O₃ sensitivity in the tropical troposphere. In the absence of lightning, chemistry was NO_x-sensitive, while it was strongly VOC-sensitive in the presence of lightning, independent of the exact location in the tropical region.

These results are in line with our previous findings in the upper tropical troposphere, which were based entirely on modeling simulations (Nussbaumer et al., 2023). This underlines effectively that $\alpha(\text{CH}_3\text{O}_2)$ is a powerful metric for identifying O₃ sensitivity and it is applicable both to modeled data and in situ observations. It also shows that NO_x is the predominant factor determining O₃ sensitivity and in the tropics its major source is lightning, which in turn depends on the time of year and the distance to tropical landmasses. Photochemical O₃ formation is capped by the availability of peroxy radicals in areas impacted by lightning. From this, we conclude that potential increases in lightning in these regions will likely not impact the amount of O₃, given that levels of peroxy radicals remain unchanged. In turn, increases in lightning in regions that are currently not or only mildly impacted by lightning might lead to increases of O₃ levels up to a factor of 2, which could strongly impact the radiative forcing (especially at high altitudes). The remote tropical lower troposphere currently has only a small number of NO sources. This could change in the future if biomass burning events would become more frequent with increasing temperature and decreasing precipitation and if countries in the Global South increase NO_x emissions associated with the expansion of their economies. Combined with NO_x-sensitive O₃ chemistry, this would lead to strong increases of O₃ levels, which could locally harm plants and human health or, given the lifetime of O₃ of a few weeks, be transported to areas where it has adverse effects.

Looking into the future, further research should investigate the changing role of NO_x in tropospheric O₃ chemistry. While we can say that NO_x is the most important driver of O₃ sensitivity, future changes and North-South re-locations in NO_x emissions, such as expected changes in emissions from anthropogenic combustion processes or increases in biomass burning, will profoundly influence tropospheric photochemistry, and in turn air quality and climate change.

Data Availability Statement

The data set for the OMO campaign can be obtained from the HALO database (last access: 23.10.2023) (Deutsches Zentrum für Luft- und Raumfahrt (DLR), 2021). The ATom data set is available at Wofsy et al. (2021) (last access: 15.09.2023). The data sets for CAFE Africa and CAFE Brazil can be accessed at Nussbaumer et al. (2024).

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